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Applications of Scanning Tunneling Microscopy to Electrochemistry

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Our efforts through the last contract period have involved the fundamental study of the STM imaging process, the investigation of the use of partially insulated STM tips as ultramicroelectrodes,[1,2] and applications of STM for the generation of lithographic features.[3] STM investigations of conducting polymers dispersed on graphite surfaces and doped with I_2 revealed that, although the conducting backbone of the polymer could be imaged under a range of tunnelling conditions, the non-conducting side groups of the polymer were not imaged. These images represent the first atomic resolution images of polymers, and studies of this type, involving the simultaneous imaging of nominally conducting and non-conducting groups, should prove essential in developing a theoretical understanding of the contrast mechanisms which dominate the imaging of individual adsorbed molecules with STM. Studies of ultramicroelectrodes, fabricated initially as partially insulated STM tips for use in solutions containing significant concentrations of electroactive species, have revealed the possibility of fabricating electrodes as small as one nanometer in diameter. Such tips, assuming a reproducible and well defined exposed metal area, may be used to make fundamental measurements of electrochemical processes,[4] such as the electron transfer rate constant for $Ru(NH_3)_6^{3+/2+}$ redox couple. The results of these investigations are currently being carefully reproduced in our laboratories, and only after intense scrutiny will it be possible to fully assess the utility of this new method of ultramicroelectrode fabrication. The final aspect of this work has been the systematic study of process of surface nanolithography on graphite using STM methods. In these experiments, a short bias pulse, typically 20μs in duration and 4V in amplitude, is superimposed on the normal tunneling bias of ~100mV, resulting in the generation of a small ~40Å pits in the surface. In contrast to earlier studies performed in air or other gaseous environment,[5] a reproducible amplitude threshold for feature generation is observed when the experiment is carried out in pure water.[3] This threshold has been determined to be 4.0 ± 0.2 V. Further, application of a threshold pulse under water has been found to generate a new type of domed feature. This domed feature has the one unusual property, that although it remains stable for extended periods of tunneling at biases up to 500mV, application of a second bias pulse of only 200mV on one of these domed features will convert it to the familiar pit feature. We believe that both the pits and domes may be converted into sites for the chemical linkage of individual molecules on an otherwise flat and ordered region of a surface.[6] This application would have widespread use for the imaging of large biological molecules which cannot typically be found isolated on a surface.

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